(54) Process for producing phase retarder from a thermoplastic resin film or sheet.

(57) For producing a phase retarder, a thermoplastic film or sheet having intrinsic birefringence and preferably of excellent transparency, e.g. a polycarbonate, is subjected to thermal relaxation at a temperature not lower than its glass transition temperature and lower than its melting point; preferably at from Tg to (Tg + 50°C), so as to shrink it in the direction of its stretching axis (or main stretching axis after unbalanced biaxial stretching), while suppressing its expansion in a direction parallel to the surface of the film or sheet and approximately perpendicular (60-120° angle) to the stretching axis.

The resultant phase retarder film or sheet is used on a liquid crystal display device.

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The present invention relates to a process for producing a phase retarder film or sheet used in liquid crystal display devices.

Phase retarder films or sheets each comprising a uniaxially oriented thermoplastic resin film or sheet have been used as optical compensators to enhance the display qualities of liquid crystal display devices.

A STN type liquid crystal display device using such phase retarder film or sheet as optical compensator is advantageous in that it is lighter in weight, thinner and less expensive, but disadvantageous in that it has a narrow viewing angle characteristic and exhibits a low contrast ratio as compared with a STN double cell type liquid crystal display device using a liquid crystal cell as optical compensator. These disadvantages have been considerably eliminated by, for example, laminating two plies of phase retarder films or sheets, but the viewing angle characteristic has not reached a satisfactory level.

The viewing angle characteristic of a liquid crystal display device using phase retarders as optical compensators depends greatly not only upon the angular dependence of the birefringence of the liquid crystal cell used therein but also upon the angular dependence of the birefringence (i.e. retardation) of the phase retarder. In conventional phase retarders, it is known that lower angular dependence of retardation gives a superior result. The angular dependence of retardation of a phase retarder film or sheet is expressed by the retardation ratio R_{40}/R_0. In this case, the retardation R_{40} is a value measured with the phase retarder film or sheet being tilted by 40° from the horizontal condition by rotating around an axis which corresponds to the slow axis if the phase retarder consists of a thermoplastic resin having a positive intrinsic birefringence, or to the fast axis if the phase retarder consists of a thermoplastic resin having a negative intrinsic birefringence; the retardation R_0 is a value measured with the phase retarder film or sheet not being tilted (i.e. arranged horizontally); and the measurement is made using a polarizing microscope equipped with a Sénarmont compensator. As the retardation ratio of a phase retarder becomes closer to 1, its angular dependence of retardation becomes lower.

In order to reduce the angular dependence of retardation of a phase retarder film or sheet, there have been proposed, for example, the following methods.

JP-A-2-16024 describes stretching a film whose molecules are oriented in a direction normal to the film surface.

JP-A-2-191904 discloses shrinking a film in a direction perpendicular to the stretching axis at the time of the uniaxial stretching.

JP-A-285303 discloses stretching a film produced from a molten polymer or a polymer solution under an electric field applied.

None of these methods, however, is satisfactory for mass production.

We have made an extensive study in order to solve the above problems. As a result, we found that a phase retarder film or sheet having a low angular dependence of retardation can be produced by subjecting a stretched thermoplastic resin film or sheet to thermal relaxation to shrink it in the stretching axis direction while suppressing its expansion in a direction parallel to its surface and perpendicular to the stretching axis.

A stretched thermoplastic resin film or sheet shrinks in the stretching direction when it is subjected to thermal relaxation in an unrestricted condition at a temperature not lower than the glass transition temperature of the thermoplastic resin. During this thermal relaxation, the film or sheet tends to expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, because the film or sheet has a neck-in (shrinkage) generated during the stretching, in the direction parallel to the film or sheet surface and perpendicular to the stretching axis.

When a stretched film or sheet is subjected to thermal relaxation while suppressing its expansion (length increase) in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, to a length smaller than that obtained in an unrestricted condition, the length in the stretching axis direction shrinks and the thickness of the film or sheet expands and exhibits improved angular dependence of retardation.

Herein, the term "stretching axis" refers to an axis of uniaxial stretching in the case of uniaxial stretching, and to an axis of main stretching in the case of unbalanced biaxial stretching.

"Perpendicular to stretching axis" refers to an angle of 60-120° to the stretching axis. Suppression of expansion in a direction of, in particular, 85-95° to the stretching axis is preferable in view of the improvement in angular dependence of retardation. Suppression of expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, as compared with the suppression in other directions, gives higher improvement in angular dependence of retardation.

"Suppression of expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis" refers to keeping the expansion in said direction substantially at zero, i.e. keeping constant the length of the film or sheet in said direction and further making the expansion in said direction smaller than the level obtained when the film or sheet is subjected to thermal relaxation in an unrestricted condition until a desired R_0 value

is obtained.

The method used for suppressing the expansion of a stretched film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, during the thermal relaxation, is not critical. The following are examples of this method.

(1) Contacting a film or sheet with a plate (e.g. a hot plate) and utilizing the frictional force generated by the contact for suppression of the expansion of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

(2) Arranging a film or sheet between a pair of parallel walls having a given distance between them, in such a manner that the film or sheet surface becomes perpendicular to the walls and the stretching axis of the film or sheet becomes parallel to the walls and thereby suppressing the expansion of the film or sheet in a direction parallel to its surface and perpendicular to the stretching axis, to a length not larger than the distance between the walls.

(3) Arranging a film or sheet in a frame having a structure in which the film or sheet is not allowed to expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis and thereby suppressing the expansion of the film or sheet in said direction.

Of these methods, there is preferred the methods (2) and (3).

Thus, by subjecting a film or sheet to thermal relaxation while suppressing the expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, there can be easily obtained a thermoplastic resin film or sheet satisfying the following formula:

$$0.900 < R_{40}/R_0 < 1.100$$

Wrinkles may be generated when a film or sheet is subjected to thermal relaxation while suppressing the expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis. In such cases, the thermal relaxation is preferably conducted while applying an appropriate pressure to the film or sheet surface.

The method used for conducting the thermal relaxation while applying an appropriate pressure perpendicularly to the film or sheet surface, is not critical. It can be any method provided that the heating of and the pressure application to the film or sheet can be conducted simultaneously. The following are examples of this method.

(1) Arranging a film or sheet in a frame having a structure in which the film or sheet is not allowed to stretch in a direction parallel to its surface and perpendicular to the stretching axis,

mounting a weight having the same bottom surface shape as the film or sheet surface, on the film or sheet, and conducting the thermal relaxation of the film or sheet while applying a pressure to the film or sheet surface.

(2) Interposing a film or sheet between releasable films, tightly winding them around a cylindrical material so that the direction parallel to the surface and perpendicular to the stretching axis of the film or sheet becomes the same as the circumferential direction of the cylindrical material, to apply a pressure uniformly to the film or sheet surface, and conducting the thermal relaxation of the film or sheet under a condition that both ends of the film or sheet are fixed so as not to allow the expansion of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

By subjecting a stretched thermoplastic resin film or sheet to thermal relaxation while applying a pressure thereto so that no wrinkle is generated in the film or sheet and there occurs increase of film or sheet thickness, there can be obtained a thermoplastic sheet or film satisfying the following formula and having no wrinkles:

$$0.900 < R_{40}/R_0 < 1.100$$

A pressure of 0.1 g/cm^2 to 10 kg/cm^2 is generally applied in view of the uniformity of the film or sheet after thermal relaxation and the relaxation rate.

The stretched thermoplastic resin film or sheet has no restriction as to its orientation provided that it can, during the thermal relaxation, shrink in the stretching axis direction and expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

The method of production of such a film or sheet is not critical. It can be produced, for example, by preparing an unstretched film or sheet by a known method such as solution casting, press molding or extrusion and then stretching the unstretched film or sheet by a known method, such as tentering, stretching between rolls or rolling.

In view of, for example, the molecular orientation in the film or sheet thickness direction during thermal relaxation and the uniformity of in-plane retardation of the film or sheet, it is preferred that a film or sheet be prepared by solution casting and then subjected to longitudinal uniaxial stretching between rolls.

The temparature at which the stretched thermoplastic resin film or sheet is relaxed thermally can be any temperature which is not lower than the glass transition temperature (Tg) of the thermoplastic resin and is lower than the melting point (Tm)

and permits the thermal relaxation of the thermoplastic resin film or sheet. The temperature of thermal relaxation varies depending upon the Tg and Tm of the resin used, but is preferably in the range of Tg to (Tg + 50°C) in view of, for example, the control of in-plane retardation and the molecular orientation in thickness direction.

In conducting the thermal relaxation of a stretched thermoplastic resin film or sheet while applying a pressure to its surface, a cushioning medium may be used in order to reduce the unevennesses in temperature and pressure. Such a medium enables the uniform transfer of temperature and pressure to the film or sheet via the cushioning medium.

It is also possible to interpose a stretched thermoplastic resin film or sheet between releasable materials (e.g. releasable polyester films) or to coat the surface of said film or sheet with a lubricant (e.g. silicone oil or molten surfactant), in order to enhance the transformation rate or uniformity in transformation rate, of said film or sheet during the thermal relaxation.

The thermoplastic resin used for preparation of a stretched thermoplastic resin film or sheet is not critical as long as it has intrinsic birefringence. However, it preferably has excellent optical properties (e.g. excellent transparency).

As the thermoplastic resin, there can be used, for example, thermoplastic resins having positive intrinsic birefringence, such as a polycarbonate, polysulfone, polyarylate, polyethersulfone or cellulose diacetate, and thermoplastic resins having negative intrinsic birefringence, such as polystyrene, α-methylpolystyrene, polyvinylpyridine, polyvinylnaphthalene or polymethyl methacrylate. Of these, a polycarbonate is preferred in view of its transparency, heat and humidity resistance and expression of birefringence.

The present invention permits easy industrial production of a phase retarder which is low in angular dependence of retardation. A liquid crystal display device having the phase retarder(s) mounted thereon shows a significantly improved viewing angle characteristic.

We refer also to the disclosure of Japanese Patent Application No. 03-324644.

The present invention is hereinafter illustrated by the following specific examples.

Example 1

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched to a 2.1-fold length at 184°C by longitudinal uniaxial stretching to obtain a stretched film of thickness = 98 μm, R_0 = 867 nm and R_{40}/R_0 = 1.108. The stretched film was cut into a size of 9.9 cm

(direction perpendicular to stretching axis) x 2.4 cm (stretching axis direction), and the cut film was placed in a frame having such a temperature in which the cut film was not allowed to expand in a direction parallel to the film surface and perpendicular to the stretching axis. On the cut film in the frame was mounted a weight having the same bottom surface shape as the cut film shape, to apply a pressure of 70 g/cm² uniformly on the film surface in a direction perpendicular to the film surface. Under this condition, the stretched film was subjected to thermal relaxation at 165°C for 120 minutes while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 9.9 cm (direction perpendicular to stretching axis) x 2.0 cm (stretching axis direction), thickness = 120 μm, R_0 = 445 nm, and R_{40}/R_0 = 1.000.

Example 2

The same stretched film as in Example 1 was cut into a size of 9.9 cm (direction perpendicular to stretching axis) x 2.4 cm (stretching axis direction), and the cut film was placed in a frame having such a structure in which the cut film was not allowed to expand in a direction parallel to the film surface and perpendicular to the stretching axis. On the cut film in the frame was mounted a weight having the same bottom surface shape as the cut film shape, to apply a pressure of 235 g/cm² uniformly on the film surface in a direction perpendicular to the film surface. Under this condition, the stretched film was subjected to thermal relaxation at 165°C for 180 minutes while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 9.9 cm (direction perpendicular to stretching axis) x 2.1 cm (stretching axis direction), thickness = 118 μm, R_0 = 586 nm, and R_{40}/R_0 = 1.047.

Example 3

The same stretched film as in Example 1 was cut into a size of 9.9 cm (direction perpendicular to stretching axis) x 2.4 cm (stretching axis direction), and the cut film was placed in a frame having such a structure in which the cut film was not allowed to expand in a direction parallel to the film surface and perpendicular to the stretching axis. On the cut film in the frame was mounted a weight having the same bottom surface shape as the cut film shape, to apply a pressure of 87 g/cm² uniformly on the film surface in a direction perpendicular to the film

surface. Under this condition, the stretched film was subjected to thermal relaxation at 170°C for 120 minutes while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 9.9 cm (direction perpendicular to stretching axis) × 2.1 cm (stretching axis direction), thickness = 122 μm, R_0 = 519 nm, and R_{40}/R_0 = 1.059.

Example 4

A polycarbonate film of 200 μm in thickness, obtained by solvent casting was stretched to a 1.1-fold length at 190°C by longitudinal uniaxial stretching to obtain a stretched film of thickness = 187 μm, R_0 = 613 nm and R_{40}/R_0 = 1.124. The stretched film was cut into a size of 9.9 cm (direction perpendicular to stretching axis) × 2.4 cm (stretching axis direction), and the cut film was placed in a frame having such a structure in which the cut film was not allowed to expand in a direction parallel to the film surface and perpendicular to the stretching axis. On the cut film in the frame was mounted a weight having the same bottom surface shape as the cut film shape, to apply a pressure of 63 g/cm² uniformly on the film surface in a direction perpendicular to the film surface. Under this condition, the stretched film was subjected to thermal relaxation at 165°C for 120 minutes while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 9.9 cm (direction perpendicular to stretching axis) × 2.2 cm (stretching axis direction), thickness = 200 μm, R_0 = 351 nm, and R_{40}/R_0 = 1.035.

Example 5

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched to a 1.1-fold length at 178°C by longitudinal uniaxial stretching to obtain a stretched film of thickness = 170 μm, R_0 = 650 nm and R_{40}/R_0 = 1.100. The stretched film was cut into a size of 30 cm (direction perpendicular to stretching axis) × 20 cm (stretching axis direction). The cut film was interposed between two same releasable films (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). Thereon was mounted a metal plate and a pressure of 4.5 g/cm² was applied uniformly on the film surface in a direction perpendicular to the film surface. Under this condition, the stretched film was subjected to thermal relaxation at 153°C for 120 minutes while suppressing

the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 30.85 cm (direction perpendicular to stretching axis) × 18.8 cm (stretching axis direction), thickness = 185 μm, R_0 = 200 nm, and R_{40}/R_0 = 1.063.

Example 6

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 138 μm, R_0 = 619 nm and R_{40}/R_0 = 1.112. The stretched film was cut into a size of 200 cm (direction perpendicular to stretching axis) × 12 cm (stretching axis direction). The cut film was interposed between two same releasable films (200 cm × 15 cm) (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). The resultant sandwich, together with a cushioning medium (200 cm × 15 cm) covered with flannel at both sides, was tightly wound around an aluminum pipe of 9 cm (diameter) × 3 mm (wall thickness). In this case, the polycarbonate film was fixed at the ends to prevent the expansion in a direction parallel to the film surface and perpendicular to the stretching axis. Under this condition, the stretched film was subjected to thermal relaxation at 152°C for 25 hours while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 200 cm (direction perpendicular to stretching axis) × 11.5 cm (stretching axis direction), thickness = 158 μm, R_0 = 421 nm, and R_{40}/R_0 = 0.978.

Example 7

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 148 μm, R_0 = 990 nm and R_{40}/R_0 = 1.167. The stretched film was cut into a size of 200 cm (direction perpendicular to stretching axis) × 12 cm (stretching axis direction). The cut film was interposed between two same releasable films (200 cm × 15 cm) (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). The resultant sandwich, together with a cushioning medium (200 cm × 15 cm) covered with flannel at the both sides, was tightly wound around an aluminum pipe of 9 cm (diameter) × 3 mm (wall thickness). In this case, the polycarbonate film was fixed at the ends to prevent the expansion in a direction parallel to the film surface and perpendicular to the stretching axis. Under this condition, the stretched film was

subjected to thermal relaxation at 153°C for 25 hours while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 200 cm (direction perpendicular to stretching axis) x 10.2 cm (stretching axis direction), thickness = 182 μm, R_0 = 467 nm, and R_{40}/R_0 = 1.007.

Example 8

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 160 μm, R_0 = 1333 nm and R_{40}/R_0 = 1.110. The stretched film was cut into a size of 200 cm (direction perpendicular to stretching axis) x 12 cm (stretching axis direction). The cut film was interposed between two same releasable films (200 cm x 15 cm) (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). The resultant sandwich, together with a cushioning medium (200 cm x 15 cm) covered with flannel at the both sides, was tightly wound around an aluminum pipe of 9 cm (diameter) x 3 mm (wall thickness). In this case, the polycarbonate film was fixed at the ends to prevent the expansion in a direction parallel to the film surface and perpendicular to the stretching axis. Under this condition, the stretched film was subjected to thermal relaxation at 153°C for 25 hours while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase retarder film of size = 200 cm (direction perpendicular to stretching axis) x 10.1 cm (stretching axis direction), thickness = 198 μm, R_0 = 692 nm, and R_{40}/R_0 = 0.954.

Comparative Example 1

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched to a 2.1-fold length at 190°C by longitudinal uniaxial stretching. The resultant stretched film had thickness = 93 μm, R_0 = 589 nm and R_{40}/R_0 = 1.114.

Comparative Example 2

A polycarbonate film of 185 μm in thickness, obtained solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 137 μm, R_0 = 619 nm and R_{40}/R_0 = 1.112. The stretched film was cut into a size of 10 cm (direction perpendicular to stretching axis) x 10 cm (stretching axis direction). The cut film was

subjected to thermal relaxation at 153°C for 2 hours on the releasable films (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). As a result, there was obtained a phase retarder film of size = 10.15 cm (direction perpendicular to stretching axis) x 9.65 cm (stretching axis direction), thickness = 141 μm, R_0 = 406 nm, and R_{40}/R_0 = 1.109.

Comparative Example 3

A polycarbonate film of 185 μm in thickness, obtained solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 160 μm, R_0 = 1333 nm and R_{40}/R_0 = 1.110. The stretched film was cut into a size of 10 cm (direction perpendicular to stretching axis) x 10 cm (stretching axis direction). The cut film was subjected to thermal relaxation at 153°C for 2 hours on the releasable films (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). As a result, there was obtained a phase retarder film of size = 10.4 cm (direction perpendicular to stretching axis) x 9.1 cm (stretching axis direction), thickness = 169 μm, R_0 = 621 nm, and R_{40}/R_0 = 1.113.

Comparative Example 4

A polycarbonate film of 185 μm in thickness, obtained solvent casting was stretched by transverse uniaxial stretching to obtain a stretched film of thickness = 137 μm, R_0 = 619 nm and R_{40}/R_0 = 1.112. The stretched film was cut into a size of 10 cm (direction perpendicular to stretching axis) x 10 cm (stretching axis direction). The cut film was subjected to thermal relaxation at 158°C for 4 minutes on the releasable films (Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co., Ltd.). As a result, there was obtained a phase retarder film of size = 10.1 cm (direction perpendicular to stretching axis) x 9.65 cm (stretching axis direction), thickness = 141 μm, R_0 = 415 nm, and R_{40}/R_0 = 1.118.

Claims

1. A process for producing a phase retarder film or sheet, which comprises subjecting a stretched thermoplastic resin film or sheet to thermal relaxation at a temperature not lower than the glass transition temperature of the thermoplastic resin so as to shrink the film or sheet in the direction of its stretching axis or main stretching axis in the case of an unbalanced biaxially stretched film or sheet, while suppressing the expansion of the film or sheet in a direction parallel to the film or sheet

surface and approximately perpendicular to the stretching axis.

2. A process according to Claim 1, wherein the thermal relaxation is conducted while keeping constant the length of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

3. A process according to Claim 1, wherein the thermal relaxation is conducted while applying a pressure in a direction perpendicular to the film or sheet surface.

4. A process according to Claim 2, wherein the length of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis is kept constant by arranging the film or sheet in a frame having a structure in which the film or sheet is not allowed to expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis of the film or sheet, thereby suppressing the expansion of the film or sheet in said direction.

5. A process according to any preceding claim, wherein the temperature of the thermal relaxation is in the range of the transition temperature of the thermoplastic resin to 50°C above said temperature.

6. A process according to any preceding claim, wherein said thermoplastic resin is a polycarbonate.

7. A liquid crystal display having mounted thereon a phase retarder film or sheet made by a process as claimed in any preceding claim.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 482 620 (NITTO DENKO CORPORATION) * page 3, line 38 - page 4, line 11 * ---	1,6,7	B29C61/02 B29C71/02 G02B5/30 G02F1/1335
A	DATABASE WPIL Week 9019, Derwent Publications Ltd., London, GB; AN 90-143316 & JP-A-2 089 006 (FUJI PHOTO FILM KK) 29 March 1990 * abstract * -----	1,6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B29C
G02B
G02F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 MARCH 1993	LANASPEZE J.P.Y.

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